

Spectroscopy of the interaction of a low-energy electron beam with organic luminescent molecules

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Contents

1. Introduction	173
2. Spectroscopic methods for studying electron-molecule interactions	174
2.1 Electron energy loss spectroscopy; 2.2 Luminescence properties; 2.3 Positive molecular ions; 2.4 Negative molecular ions	
3. Conclusions	181
References	181

Abstract. We present a brief review of the results of spectroscopic studies of the interaction of a beam of low-energy mono-kinetic tunable-energy electrons with organic luminescent molecules. Data are presented on elastic scattering, the excitation of vibrational and electronic transitions, luminescence properties, and the formation of positive and negative ions for a number of molecules. It is shown that the passage of electrons through the gaseous and thin-film phases of organic samples is close in nature. For all processes, except the excitation of triplet transitions and the formation of negative ions, the dipole interaction prevails, even in the near-threshold region. The results of the conducted research will be useful for understanding the conversion of electron energy by organic molecules in electronics, where the direct study of elementary processes is very difficult, as well as in biology and plasma chemistry.

Keywords: organic molecules, excitation, electrons, luminescence, ionization, energy loss spectra

1. Introduction

Organic luminescent molecules enjoy a wide range of applications in electronics, biology, and other fields. Among the huge number of organic molecules, luminescent molecules are the most stable due to the fact that the energy absorbed by them is partially emitted in the form of an energy quantum and is not lost in the molecule, leading to the weakening of bonds and destruction of molecules. Organic electroactive molecules with electron-donating or electron-withdrawing

properties are often used in molecular electronics devices [1, 2] due to the strong effect of their electroactivity on the properties of charge transfer in thin films formed on the basis of such molecules. The principle of operation of molecular electronic devices is based on the passage of electrons through a molecular medium. The interaction of molecules with electrons of various energies leads to the formation of excited and ionized molecules [3, 4]. Many of these processes are resonant, and most of them can also be observed in biological molecules [5–7], although they are, as a rule, far less stable. In this regard, it is of interest to study the interaction of low-energy electrons with organic luminescent molecules of various structures. The action of high-energy electrons is largely due to the secondary electrons produced in the course of ionization [8].

However, in general, there is too little information about electron interactions with molecules of organic compounds (compared with information about the interaction of electrons with atoms [9] and simple molecules [10, 11]), especially for luminescent organic compounds, and photoexcitation, with the result that there is still no complete understanding of the interaction of electrons with large organic molecules. This is due to several reasons, the main one being, as a rule, the low stability of organic molecules, which they therefore break up into fragments that are investigated. Initially, the materials are in a solid state, and, in order to conduct research, they must be evaporated and maintained at an appropriate temperature; therefore, there are few luminescence studies of this kind. In addition, electrons of sufficiently high energy interact simultaneously with all components of the medium under excitation, for example, with a solvent and a dissolved substance, or with a matrix and an activator, which often gives rise to reactions between them.

This paper provides a brief review of research on the interaction of low-energy electrons (with energies from zero to 100 eV, and in some cases up to 500 eV) with organic luminescent electroactive molecules, mainly in the gas phase, which were performed primarily by the authors of this paper. Some of the work was carried out jointly with other organizations. Such studies became possible by virtue of the scientific school of N A Borisevich on the study of the luminescence properties of molecules in the gas phase. The

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results of the studies carried out will be useful in electronics, where a direct study of elementary processes is very difficult, and in biology when studying the interaction with matter [12].

Excitation by electron impact makes it possible not only to study the features of this excitation, but also to obtain new information that cannot be extracted with optical excitation. Investigations reliant on excitation by electron impact make it possible to determine a more complete structure of energy levels in a wide range of energies, the properties of molecular electron shells, as well as transport and molecular characteristics. The most direct methods for studying electron-molecule interactions are the spectroscopic ones: electron energy loss spectroscopy, luminescence spectroscopy, and mass spectroscopy. Mass spectroscopy and high-resolution electron energy loss spectroscopy are used much more widely than luminescence spectroscopy. Luminescent organic molecules can be studied either in an ultrathin film or in the gas phase. Ultrathin molecular films are formed on a metal substrate, and therefore the study of their luminescent properties is difficult due to the significant quenching of luminescence by the metal [13], while the study of luminescent properties in the gas phase gives the purest results.

2. Spectroscopic methods for studying electron-molecule interactions

Unlike photons, which are completely absorbed, electrons, when passing through a substance, lose energy in portions in a series of successive Coulomb, polarization, and exchange interactions mainly with bound electrons of substance molecules, causing excitation of vibrational, singlet, and triplet electronic states, ionization, or attachment in many molecules before they completely lose their energy. The amount of energy transferred depends on the speed of the electron and the impact parameter, as well as on the angle of interaction with the molecule. Therefore, the result of the interaction is determined both by the electron-molecule kinetic system and by the internal properties of the molecules. Electron-molecule interaction can be studied in the most direct way from the results of the action on the molecule with the use of spectroscopic techniques.

Consider the main characteristics of electron-molecule interactions and information that can be obtained from spectroscopic studies for luminescent organic molecules of various classes (aromatic, heterocyclic, carbonyl- and metal-containing molecules, as well as molecules that include a heavy atom), which are active laser media or devices of molecular electronics and are of interest in biology. Luminescent molecules provide the purest results, which are not complicated by the course of several processes.

2.1 Electron energy loss spectroscopy

2.1.1 Electron energy loss spectra. One of the main characteristics of any interaction of free electrons with molecules is the electron energy loss spectrum (EELS), which shows what part of the electron energy goes to initiate the excitation of the corresponding levels. The EELS is a kind of analog of the optical absorption spectrum. The distribution over the energy lost by electrons in collisions with molecules provides information about the position of the molecules' energy levels, the intensity of scattered electrons gives the value of the interaction cross section, and the angular distribution is determined by the nature of the interaction and contains information about the properties of the excited state. When scattered by a target, the intensity of the electron beam lowers and the initially narrow electron energy distribution trans-

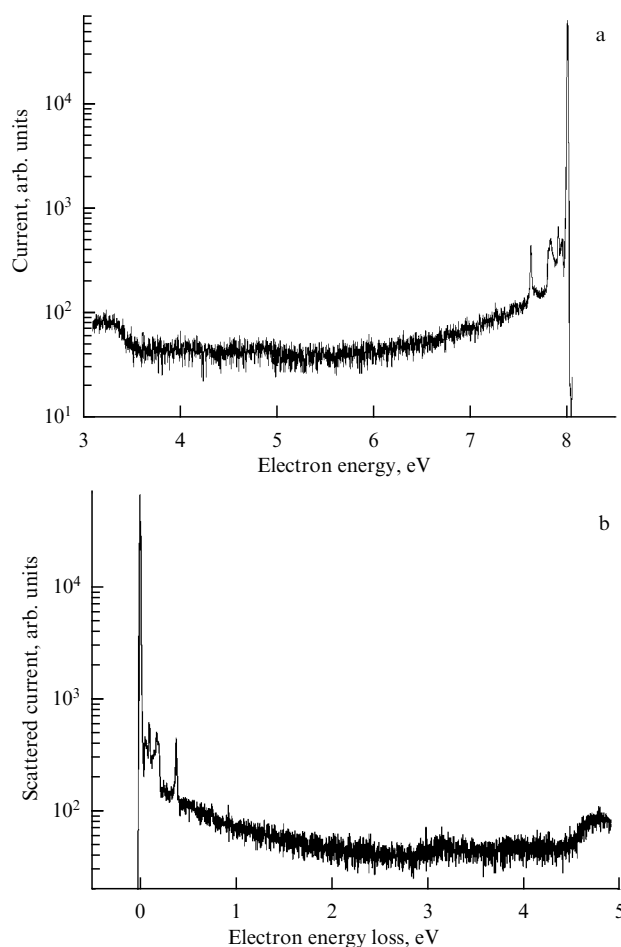


Figure 1. Electron scattering [14] (a) and energy loss (b) spectra for a thin Alq_3 film within 5 eV for an incident electron beam with an energy of 8 eV at 138 K; thickness of the Alq_3 film is 1.9 monolayers (~ 1.9 nm). Angle of incidence and scattering: 60° ; energy resolution: 10 meV.

forms into a wide spectrum, from zero to the energy of the incident electron [14] (Fig. 1a). Figure 1b [14] shows the electron energy loss spectrum in the range of 0–5 eV for tris(8-hydroxyquinolinato)aluminum (Alq_3) on a logarithmic scale along the ordinate with a resolution of 10 meV. These spectra contain an elastic scattering peak, as well as losses ΔE due to vibrational and electronic excitation. At higher values of electron energy loss, one can see the excitation of σ -states, etc. The vibrational bands are narrow, while the electronic bands are wide due to the strong electronic-vibrational-rotational interaction and a high level density. Therefore, the loss due to electronic excitation can be studied at a far lower beam monochromaticity. The figure shows the difference between the elastic and inelastic scattering peaks, which change with the incident electron energy and the angle of interaction. The intensity of vibrational bands is approximately one or two orders of magnitude lower than the intensity of the elastic scattering peak, and the intensity of electronic transitions is even lower by approximately an order of magnitude. Vibrational EELSs were obtained for ultrathin films of many molecules [12]. It is noteworthy that elastically scattered electrons change only the direction of motion but retain the ability to excite and ionize at the appropriate energy.

Figure 2a shows the loss spectra for oscillation excitation at various incident electron energies. Despite the insufficiently high resolution for recording individual vibrational

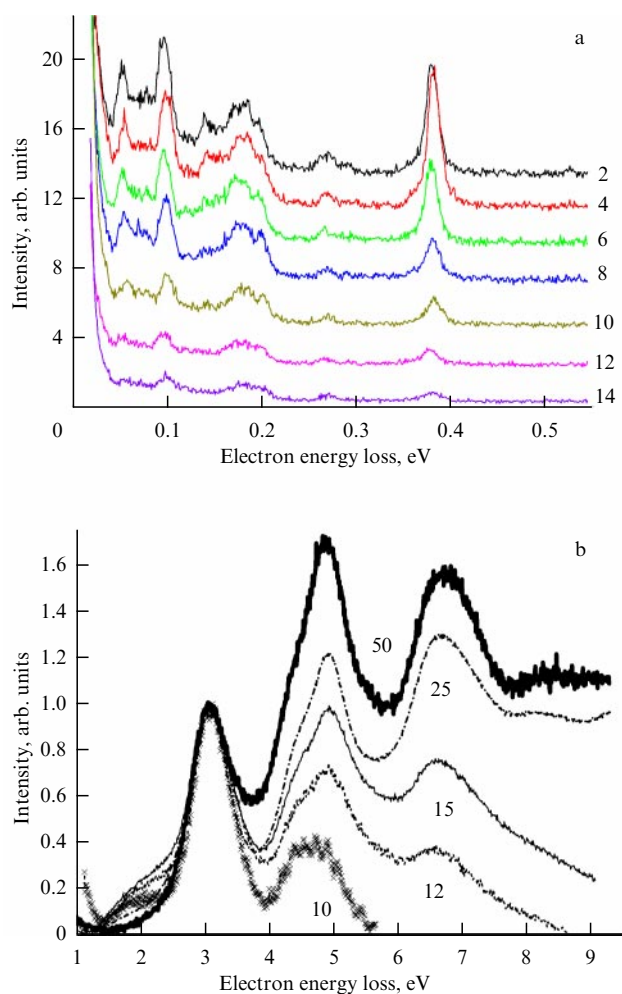


Figure 2. (a) Vibrational spectra of electron energy loss for Alq₃ film molecules (film thickness: 0.75 monolayer (~ 0.75 nm), $T = 14.2$ K) [14]. (b) Electron energy loss spectra for gas-phase 9,10-di(phenylethynyl)anthracene (DPEA) [15]. Numbers by the curves indicate electron energy in electron volts.

excitation bands, one can see a number of clearly distinguishable bands identified as 55 meV (out-of-plane deformation vibrations of the ring, Al–N), 94 meV (out-of-plane C–H deformation vibrations), 143 meV (deformation vibrations in the C–H plane), 181 meV (stretching vibrations of the ring), 194 meV (stretching vibrations of the ring), and 377 meV (stretching C–H vibrations). Vibrational spectra also even at submonolayer thicknesses, when individual molecules or their aggregates are adsorbed on the substrate, thereby indicating the high sensitivity of the method. We do well to bear in mind that selection rules forbid the excitation of the deformation vibrations of molecular bonds by the dipole mechanism when they coincide with the substrate plane. Note that electron energy loss spectroscopy on ultrathin films has gained wider acceptance [6, 12] than gas-phase studies, although each case has its own advantages and disadvantages.

The EELS in the region of electronic levels also changes significantly with increasing electron energy (Fig. 2b) [15], which is primarily manifested in an increase in the contribution of higher-lying states to the excitation. However, the intensity of some bands lowers.

In order to explain this behavior for atoms and molecules, theoretical studies of the interaction with electrons were

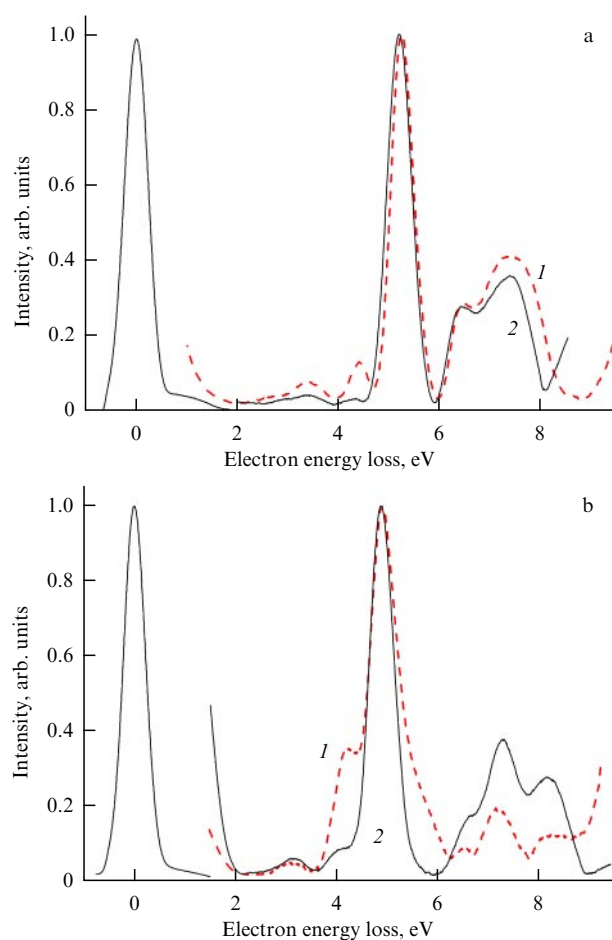


Figure 3. EELS for (a) fluorenone and (b) diiodofluorenone at electron energies of (1) 15 eV and (2) 50 eV [17].

carried out in [9, 11], the results of which can be applied to complex molecules as well. In the Born approximation [11], which is valid at energies above 50–100 eV, the incident electron can be considered a fast small external perturbation arising from the long-range dipole interaction between the incident electron and the molecular target. At such energies, the electron wavelength is small compared to the dimensions of the molecule, and the electron can be considered to interact independently with each molecule, while the scattering amplitude is equal to the sum of individually scattered waves. At low energies, especially near the excitation threshold, the perturbation of the target orbitals by the incident electron is strong. Such a perturbation and the possibility of spin exchange can lead to the excitation of optically forbidden singlet-triplet transitions. Specifically, low-energy EELSs are significantly different [3, 13, 15–18] (Figs 2b and 3), associated with the presence of forbidden singlet-triplet transitions due to so-called exchange interactions, in which the exciting electron replaces an electron of a molecule with the opposite spin. The intensity of singlet-triplet transition peaks rapidly decreases with increasing electron energy (see the low-energy band at 1.8 eV for 9,10-di(phenylethynyl)anthracene (DPEA) in Fig. 2b [15]), since such transitions are narrow resonances in character. For benzene, it was shown in [19] that the probability of these transitions, compared with the probability of singlet-singlet transitions, rises as the scattering angle θ increases from 0 to 90°. For $\theta = 90^\circ$, the cross section of singlet-triplet transitions is approximately only an order of magnitude smaller

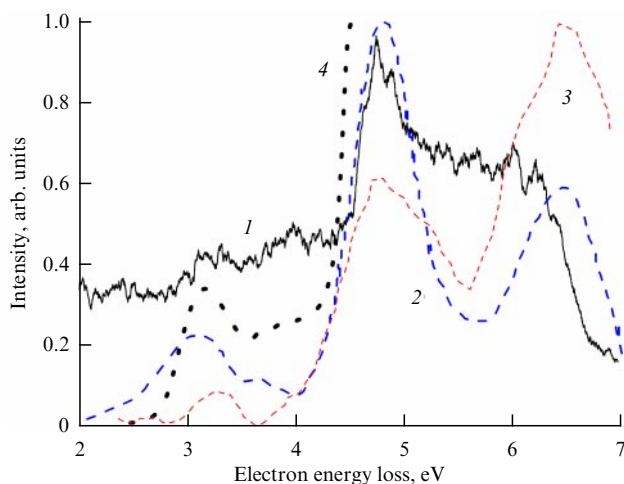


Figure 4. EELS for passing electrons: through an ultrathin film Alq_3 (two monolayers (≈ 2 nm), $T = 14.2$ K) at $E = 8$ eV (curve 1) [14], through a thick film (300 nm) at $E = 10$ eV (curve 2) [20], and through a gas at $E = 80$ keV (2) [19]. Curve 4 shows the optical absorption spectrum of a thick film.

than that of singlet-singlet ones. The most pronounced change in the singlet-triplet transition was observed for fluorenone and diiodofluorenone (see Fig. 3) [17]. One can see that the introduction of a heavy iodine atom into a fluorenone molecule entails a significant increase in the cross section of the singlet-triplet transition, which can be considered an analogue of the optical effect of a heavy atom. Near the peak of elastic scattering, one can also see the loss to vibrational excitation in the form of a wide band due to low resolution.

On the whole, we have measured the EELSs and radiative properties for many molecules in the gas phase: polyphenyls and polyacenes [20], oxazoles and oxadiazoles [21], perylene [22], naphthalimide [23], fluorene-like molecules [17, 24–26], organic complexes of europium [27], dibenzoxazolybiphenyl [28], DPEA [15], Alq_3 and triphenyldiamine [18], $\text{Ir}(\text{ppy})_3$ [16], cyanines [29], etc.

Interestingly, the electron energy loss spectra recorded in the range of electronic level excitation for the condensed and gas phases (Fig. 4) are similar to each other, thereby indicating the common nature of the interaction of low-energy electrons with organic materials in the gas and thin-film phases and the same characteristics of the electron motion in them. Moreover, the loss spectra are close to the optical absorption spectra, which is indicative of the predominantly dipole nature of the interaction, even at low electron energies. It is pertinent to note that a correct comparison of the spectra invites taking into account the concentration of molecules and the thickness of the layer through which the electron beam passes. The similarity between electron energy loss spectra in the gas and solid phases can be attributed to the fact that organic materials (unlike inorganic materials that exist due to covalent or ionic bonds of atoms throughout the solid) are formed by individual molecules bound by weak intermolecular interactions. As a consequence, there is only a small difference in energy levels and energy conversion for an individual molecule and a condensed medium, while the differences among these characteristics for inorganic compounds is enormous. Complex organic molecules often have a generalized π -electron shell, in which the π -electrons are quasi-delocalized and can easily move, which is confirmed by data on their conductivity [30].

Therefore, the properties of individual molecules can be used to describe molecular solids, as a first approximation.

2.1.2 Dependence of the excitation cross section on the electron energy. As is seen from Fig. 2a, the intensity of the bands in EELSs for vibrational levels is different at different energies. Figure 5a illustrates this dependence for different bands. As is well known [31], the excitation of vibrational transitions occurs through a dipole interaction (anisotropic, which manifests itself for transition moments perpendicular to the surface and long-range) or by an impact mechanism (quasi-isotropic and short-range). Both processes also depend on the electron energy in different ways: according to the dipole mechanism, the cross section decreases with increasing electron energy E according to the law $1/E$, and according to the impact one, it increases proportionally to E . At the same time, with increasing film thickness, the intensity of vibrations excited by the dipole mechanism increases linearly, while the intensity of those excited by the impact mechanism rapidly saturates [31]. In the case of Alq_3 , an increase in the incident electron energy results in a decrease in the intensity of almost all vibrational bands in accordance with the dipole mechanism [13]. For some bands, the dependences of the excitation cross section (the so-called excitation functions, EFs) are shown in Fig. 5a. The behavior of these functions for Alq_3 is similar to their behavior for other molecules [32]. At low electron energies, the 181 and 377 meV bands show some increase in the excitation cross section, which testifies to a parallel action of the impact mechanism.

For optically allowed electronic transitions, the cross-section maximum in the case of Alq_3 molecules (Fig. 5b) and 1,4-bis(2,5-phenyloxazolyl)benzene (POPOP) (Fig. 5c) is observed at energies exceeding the threshold energy by 3–5 times. Despite some differences, there are common features in the behavior of the dependence of the cross section on the electron energy. It is therefore possible to take advantage of the approaches developed for atoms and simple molecules. For allowed transitions, the effective excitation cross section in the Bethe–Born approximation is expressed by the formula $\sigma(E) = \sigma^{\max} \varphi(E/E_{\text{exc}}) q$ [11], where $\sigma^{\max} = 1.48 \pi a_B^2 (E_H/E_{\text{exc}})^2 f$, $\varphi(E/E_{\text{exc}}) = 2.7 (E_{\text{exc}}/E) \ln(E/E_{\text{exc}})$, a_B is the Bohr radius, E_H is the ionization energy of the H atom, E_{exc} is the threshold excitation energy, f is the transition oscillator strength, and q is the Franck–Condon factor. The function $\varphi(E/E_{\text{exc}})$ is universal within error limits. The cross section increases from the threshold value to the maximum at $E/E_{\text{exc}} \approx 4$, and then a slow decrease is observed (which qualitatively corresponds to the behavior of the dependences we measured). The same concepts can also be applied in the case of large luminescent molecules.

Comparing the experimental data for POPOP [20] and Alq_3 [13] with the corresponding curves in the Bethe–Born approximation revealed a significant difference in the maximum value of the cross section, although more accurate additive modeling [33] and the use of the jelly model showed their fairly good agreement. The absolute cross sections for the electron impact excitation of radiative states of perylene molecules were estimated using the maximum measured EF values. They amount to $3 \times 10^{-16} \text{ cm}^2$ [3], which, within the error, coincides with the cross-section values obtained with optical excitation ($2 \times 10^{-16} \text{ cm}^2$). Therefore, at the optimal electron energy (at the peak of the EF), the photon and electron excitation cross sections are approximately equal. To accurately measure the excitation cross sections, it is necessary to measure the EELS integrals over all scattering angles. It should also be noted that, after reaching the maximum, the cross section decreases faster than the

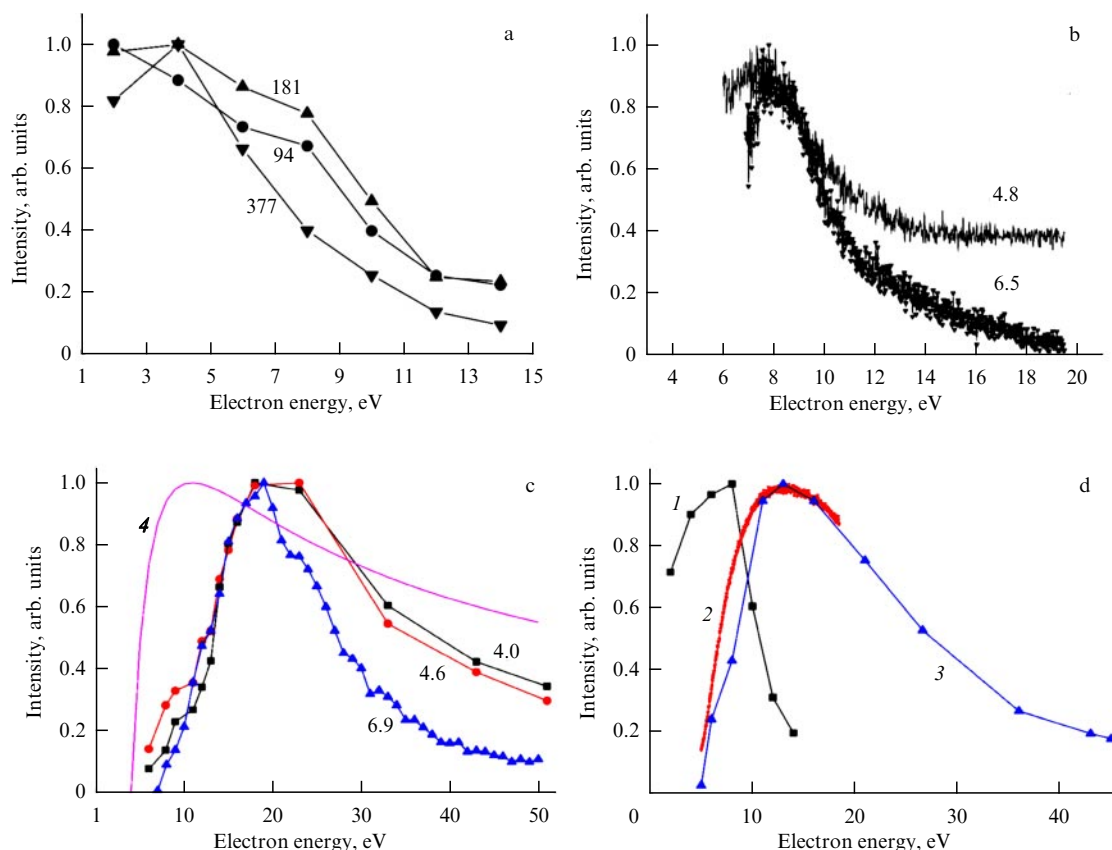


Figure 5. Dependence of the excitation cross section on electron energy: for vibrational levels (with energy indicated in meV) of the Alq₃ film [14] (a); for electronic levels (with energy indicated in eV) of Alq₃ [18] (b) and POPOP [21] (c) vapors; elastic interaction [18, 21] (d) of (1) film and (2) Alq₃ and (3) POPOP vapors. Curve 4 in Fig. 5c is the result of calculations in the Born approximation.

theoretical curve, which may be due to the contribution to the experimental curves made by singlet-triplet transitions that occur in the replacement of a molecule's electron by an incident electron when their velocities coincide. This process has a narrow-resonance character and sharply depends on the energy of electrons in atoms and simple molecules [9–11].

The elastic interaction cross section for Alq₃ and POPOP molecules (Fig. 5d) peaks at an energy of 12 eV [21]. Elastic scattering in ultrathin films (Fig. 5d) reaches its maximum value at a lower incident electron energy, at about 6–8 eV, which is apparently related to the ordered arrangement of molecules in the film. When comparing these dependences, one should also take into account the path length in the substance, which is determined by the density of molecules and the interaction cross section.

Estimates made for POPOP molecules suggest that the elastic interaction cross section at its maximum approximately corresponds to the geometric cross section [21]. The results of simulations of the total cross section of interaction with the POPOP molecule performed by the additivity method [33] showed that the contribution of exchange and polarization interactions at sufficiently high electron energies is insignificant. However, with a decrease in the electron energy, it increases significantly and can have an appreciable effect on the energy conversion by organic molecules. The inclusion of the effect of 'shadowing' of internal atoms significantly reduces the interaction cross section at relatively low energies. At high electron energies, the contribution of the inelastic interaction becomes insignificant, and the curve of the total scattering cross section coincides with the elastic interaction curve.

2.2 Luminescence properties

2.2.1 Fluorescence excitation function. The luminescence intensity also depends on the electron energy. It is well known that, although molecules are excited to different electronic states, luminescence occurs in the transition from the lower excited singlet state S_1^* , whose energy is 1–4 eV. The energy of higher states finds its way into this state due to a very fast internal conversion. The efficiency of electron energy conversion into light energy is qualitatively characterized by the dependence of the fluorescence intensity on the electron energy, or the so-called fluorescence excitation function (FEF). This function reaches its maximum value at an energy of exciting electrons that is 3–4 times higher than the threshold value, which is approximately equal to the excitation energy of the S_1^* state [3, 18, 21, 22] (Fig. 6a). A further increase in the electron energy results in a slow decrease in the fluorescence intensity. An increase in the number of nitrogen atoms in heterocyclic molecules and, accordingly, in the number of n -orbitals leads to a strong decrease in the functions after reaching the maximum [3]. Found for the FEF of carbazole, POPOP, and paraterphenyl was a slowdown in the increase in fluorescence intensity near the excitation threshold of the S_2^* singlet state.

If the glow is due to the products of decomposition of molecules, then the FEF has a much higher threshold (Fig. 6b) with a maximum in the region of 65–80 eV, indicating that this glow arises from the excitation of these products by electrons. The FEF magnitude is the result of the excitation of all electronic states for a given electron energy with the inclusion of the fluorescence quantum yield, i.e., the behavior of the FEF largely reflects the intramolecular energy exchange as

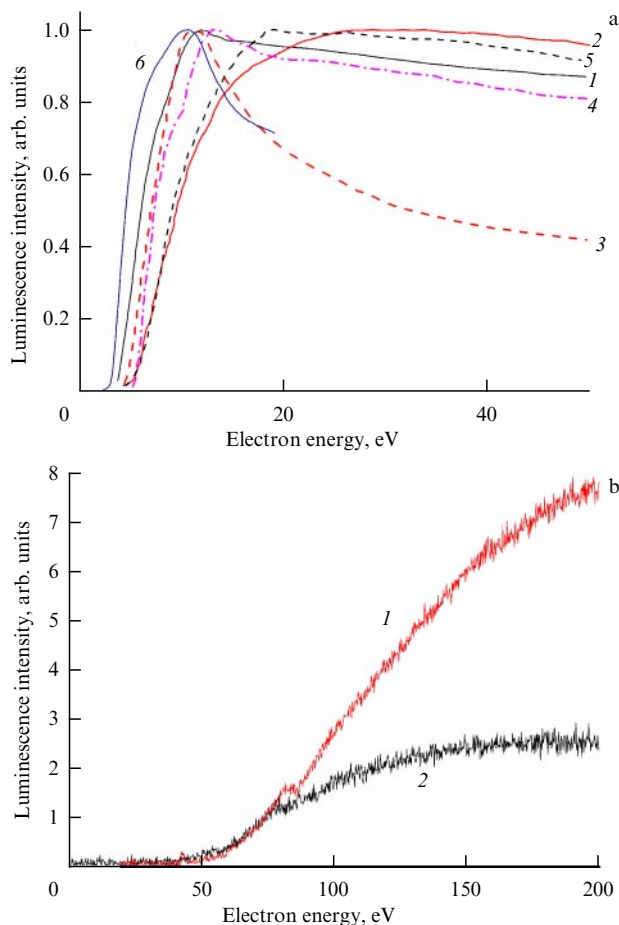


Figure 6. (a) Fluorescence excitation functions: POPOP (1), 2,5-di(biphenyl)oxazole (BBO) (2), 2,5-diphenyloxadiazole (PPD) (3), carbazole (4), para-terphenyl (5), and Alq₃ (6) [18, 21, 22, 24]. (b) Hydrogen lines in excitation of carbazole (1) and aluminum lines in excitation of Alq₃ (2) [37].

well as the efficiency of the electron-molecular interaction. Then, the fluorescence EF $W_{fl}(E)$ can be defined as [3, 22] $W_{fl}(E) = (j/e)n_0h\nu\int\sigma(E_{exc})\gamma(E_{exc})dE_{exc}$, where j is the current density, e is the electron charge, n_0 is the density of molecules, $h\nu$ is the fluorescence photon, and $\gamma(E_{exc})$ is the dependence of the fluorescence quantum yield on the electron energy.

2.2.2 Fluorescence spectra. The fluorescence spectra of organic molecules in the gas phase are an important and highly informative characteristic. They substantially depend on the store of vibrational energy E_{vib} , which is retained prior to the fluorescence event [34]. In the near-threshold excitation, the fluorescence spectrum is structured and not broadened (Fig. 7a, curve 1). As the electron energy increases, the fluorescence spectrum usually loses its vibrational structure, broadens, and shifts to the long wavelength side due to an increase in E_{vib} (Fig. 7a) [23]. Such fluorescence spectra have a vibrational structure, in contrast to the structureless spectra obtained upon optical excitation up to the second S_2^* band [35]. However, this is due to the fact that the electron-excited fluorescence spectrum forms an ensemble of molecules excited to different electronic states [3]. Specifically, the sum of the spectra of optical excitation that causes the transition to the first and second bands of perylene approximately corresponds to the spectrum obtained in the

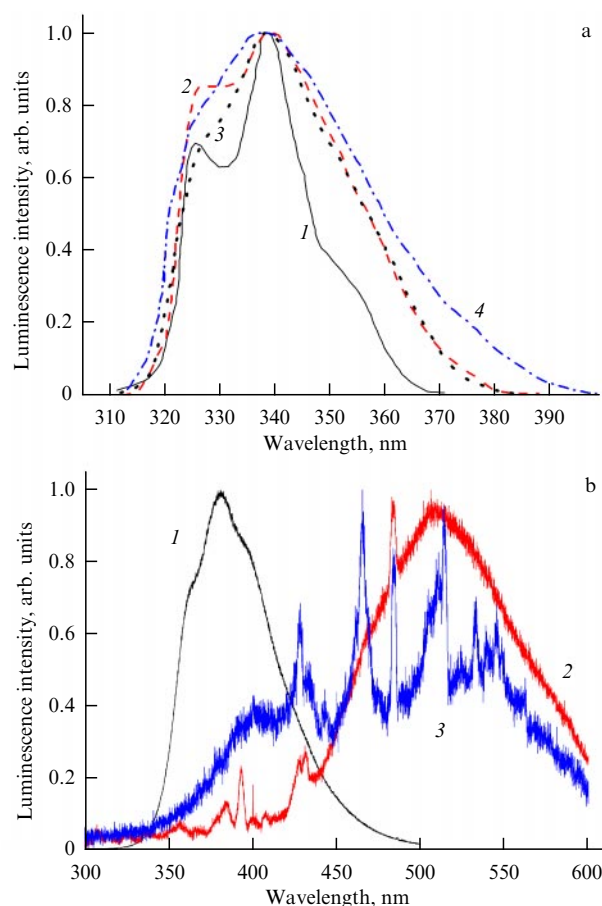


Figure 7. Vapor fluorescence spectra of (a) carbazole in excitation by electrons with energy $E_{exc} + 0.2$ eV (1), $E_{exc} + 1$ eV (2), $E_{exc} + 50$ eV (3), and $E_{exc} + 500$ eV (4) [25]; (b) POPOP (1), Alq₃ (2), and diiodofluorenone (3) in excitation by electrons with an energy of 200 eV [38].

excitation by electron impact [35]. If $E = 50$ eV or higher, then the fluorescence spectrum does not undergo strong changes (curve 3) and remains practically unchanged with a further increase in the electron energy due to the absence of differences in the EELS.

In the absence of collisions between molecules in the gas phase, the equilibrium state may not have time to set in during the lifetime of the molecule in the excited state. Then, on the basis of the above notions, it is possible to determine the overhear value ΔT (excess of the temperature of molecules over the equilibrium temperature) averaged over the ensemble of molecules using the electron ELS $\sigma(E_{exc})$ [36], $\Delta T = \int \sigma(E_{exc})\gamma(E_{exc})(E_{exc} - E_{exc}^{inv})dE_{exc} / \int C\sigma(E_{exc})dE_{exc}$, where E_{exc}^{inv} is the energy of the inversion point and C is the vibrational heat capacity. Note that the fluorescence spectra in the condensed phase do not change with the electron energy due to the effective exchange of vibrational energy with molecules in the environment, with the result that thermal equilibrium is reached in a time far shorter than the lifetime of a molecule in an excited state.

With increasing electron energy, the fluorescence spectrum can also change due to the addition of the luminescence of decomposition products, depending on the stability of the molecules (Fig. 7b) [37]. The study of the fluorescence spectra of various molecules excited by tunable-energy electrons [37] confirms the previously proposed classification of molecules according to their stability [12, 37]. Specifically, highly luminescent aromatic hydrocarbons (polyacenes, polyphe-

nyls) are the most stable, while heterocyclic compounds are less stable. Compounds containing a carbonyl group, as well as F, Cl, Br, I, S, metal atoms, and other atoms with unbound electrons, are the least stable.

2.2.3 Fluorescence kinetics. The fluorescence kinetics of free organic molecules has been little studied. Anthracene vapor fluorescence [38], which arises in irradiation by low-energy monochromatic electrons, decays exponentially. A change in the electron energy from 3.5 eV to 38 eV led to a decrease in the lifetime from 10 ± 3 ns (3.5 eV) to 6.7 ± 0.4 ns (38 eV), which is in good agreement with optical excitation data, where changing λ_{exc} from 369 nm to 216 nm reduced the fluorescence duration from 6.4 ns to 4 ns.

2.2.4 Energy yield of fluorescence. The energy yield of fluorescence is defined as the ratio of the energy emitted by a molecule in the form of a fluorescence photon to the energy absorbed in the collision with an electron. Since an electron is capable of transferring a molecule to any state, it is appropriate to discuss the average energy yield over an ensemble of molecules. The concept of the quantum yield of fluorescence is also retained in excitation by electrons, since the quantum yield is determined by the probabilities of radiative and nonradiative transitions, which are properties of the molecules themselves.

Using the EELS integrated over all scattering angles (or the total photoabsorption spectrum), we determine the average over an ensemble of molecules for the absorbed energy [3, 39] $\bar{E}_a = \int \sigma(E_{\text{exc}}) E_{\text{exc}} dE_{\text{exc}} / \int \sigma(E_{\text{exc}}) dE_{\text{exc}}$ and for the fluorescence quantum yield $\bar{\gamma} = \int \sigma(E_{\text{exc}}) \gamma(E_{\text{exc}}) dE_{\text{exc}} / \int \sigma(E_{\text{exc}}) dE_{\text{exc}}$. The fluorescence energy yield in the excitation by electrons is then $\gamma_e = \bar{\gamma} \bar{E}_a / \bar{E}_a = \bar{\gamma} \int \sigma(E_{\text{exc}}) \gamma(E_{\text{exc}}) dE_{\text{exc}} / \int \sigma(E_{\text{exc}}) E_{\text{exc}} dE_{\text{exc}}$, where \bar{E}_a is the average value of the fluorescence photon. At low energies of the incident electrons E (≤ 100 eV), the EELS depends on E , so γ_e will also be a function of E with a maximum near the excitation threshold; on the contrary, for large E , the EELS is constant and γ_e will be invariable.

2.2.5 Fluorescence polarization. Characteristic of rarefied vapors is free molecular motion, in which the angular momentum and kinetic energy are constant between collisions. Therefore, in the excitation, despite the fact that the period of free rotation of molecules is two to three orders of magnitude shorter than their lifetime in the excited state, the induced anisotropy of the orientational distribution of molecules can persist in time and manifest itself in fluorescence polarization.

We have detected the polarization of fluorescence for a number of molecules excited by a beam of monokinetic electrons with an energy varying in the range of 5–300 eV [3, 40] (Fig. 8). The electric vector of the radiation is greater in magnitude in the direction perpendicular to the direction of motion of the electron beam, although high-energy electrons (200 keV) give rise to fluorescence polarization directed along the beam [41, 42]. This fact indicates that the inelastic scattering of low-energy electrons occurs primarily perpendicular to the direction of beam motion, while the scattering of high-energy electrons coincides with it. For the substances under study, the observed maximum of fluorescence polarization approximately coincides with the maximum of the excitation function. The highest degree of fluorescence polarization (3.8%) was observed for POPOP vapors, which is lower than with optical excitation, and this detail can also be attributed to the fact that this figure is the average over the EELS, taking into account quantum yields

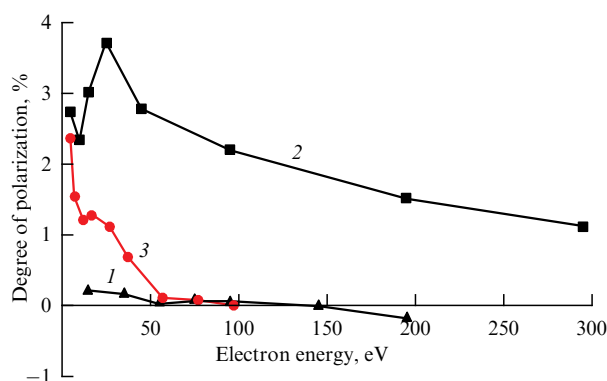


Figure 8. Dependence of the fluorescence polarization for anthracene (1), POPOP (2), and perylene (3) vapors on electron energy [40].

in the excitation to different bands. The average value of the degree of polarization over the ensemble of molecules in the excitation by an electron impact r_e can be defined as $r_e = \int \sigma(E_{\text{exc}}) r(E_{\text{exc}}) \gamma(E_{\text{exc}}) dE_{\text{exc}} / \int \sigma(E_{\text{exc}}) dE_{\text{exc}}$, where $r(E_{\text{exc}})$ is the degree of polarization in the excitation to a state with energy E_{exc} . In the case of ordered molecules, higher values of polarization can be expected.

2.3 Positive molecular ions

When the electron energy exceeds the ionization energy of the molecule, positive molecular ions are produced as a result of the interaction. The most convenient method for studying them is mass spectroscopy, in which the ratio of the particle mass m to its charge z is recorded. This method is widely used in chemistry to identify the mass of the parent ion and study the pathways of molecular fragmentation. Figure 9 shows the mass spectrum of the POPOP molecule [43]. One can see that POPOP is a very stable molecule, since the parent ion is prevalent. However, a large number of fragmentation product ions with different m/z ratios are observed in the spectrum, although the intensity of the corresponding peaks is low.

The dependence of the ionization cross section on the electron energy (Fig. 10a) [44, 45] is basically similar to the EF of optically allowed levels, with the maximum exceeding the ionization threshold by a factor of 3–4. This indicates that the ionization is predominantly dipole in nature. The presence of

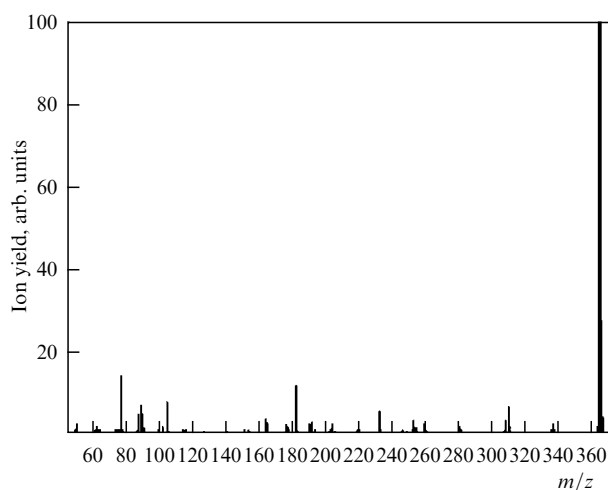


Figure 9. Mass spectrum of POPOP vapors produced under irradiation by electrons with an energy of 70 eV [43].

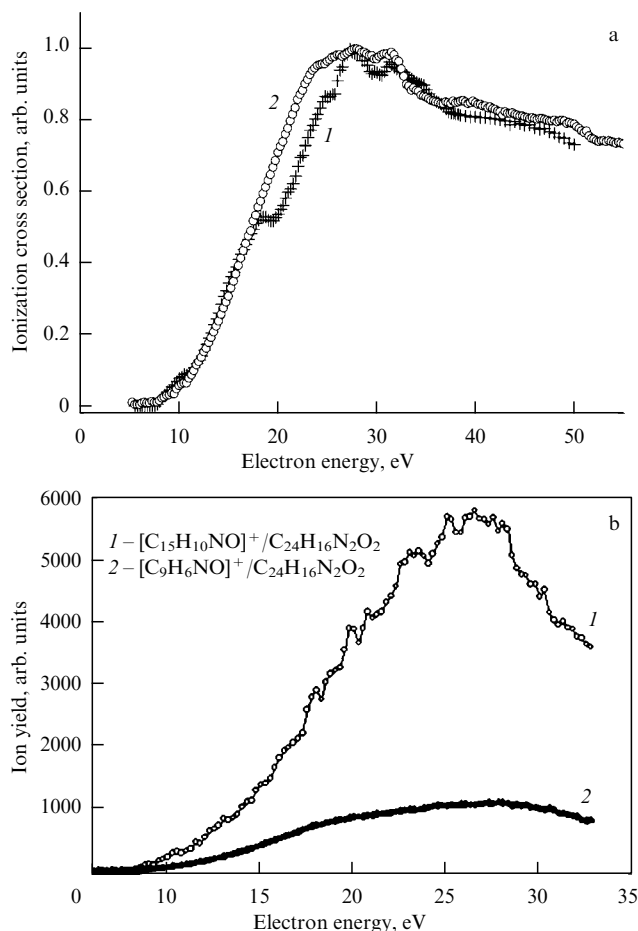


Figure 10. Energy dependences for the production of: (a) POPOP (1) and 9,10-di(phenylethynyl)anthracene (DPEA) (2) positive ions [44, 45]; (b) fragments of POPOP ions [43].

some structure suggests the possibility of the occurrence of fragment ions. The ionization probability depends rather heavily on the temperature.

According to Wannier's work [46], for the hydrogen atom, there are three zones in electron-molecular interactions: the first one is at small distances between particles (up to $\sim 1a_B$), when the interaction must be calculated quantum-mechanically; the second is at a distance between particles of the order of $100a_B$, when the Coulomb forces operate; and the third zone is where the particles hardly interact. Proceeding from this, it was determined that (i) the scattered and remote (emitted) electrons move in opposite directions, and the angular momentum of the system is equal to zero; and (ii) both electrons carry away equal parts of energy. It turns out that the energy dependence of the ionization cross section near the threshold is exponential. The exponent can range from 1.127 (the lower limit for atoms) to 4.0 for polyatomic molecules. The threshold behavior of the molecular ionization cross section is expressed as a superposition of several exponents. The ionization potentials were determined from the threshold section of this dependence. It is pertinent to note that the emitted electrons are also capable of causing the ionization and excitation of molecules, depending on their energy.

The dependence of the cross section for the appearance of ionized molecular fragments (Fig. 10b for POPOP [43]) also has a threshold, and the position of the maximum is in the same energy range as for the parent ion.

2.4 Negative molecular ions

At a low energy of the incident electron (in the range from zero to 1 eV, and sometimes even higher), the electron can stick to the molecule to form a negative ion. Such processes are also reliably studied by modified mass spectroscopy. We observed long-lived negative ions for Alq_3 and many other molecules [47–51]. This is a resonant process, with the result that the attachment is observed in a rather narrow energy range. The curve of the effective Alq_3^- yield (Fig. 11a) [47] shows that the vertical electron capture energy $E_a = 0.26$ eV. The mean lifetime of molecular negative ions with respect to autodetachment decreases almost linearly with increasing electron energy, from ~ 800 μs at zero energy to 400 μs at an electron energy of 0.8 eV. Measuring the autodetachment lifetime permits estimating the adiabatic electron affinity at ~ 1 eV in the framework of the Christophorou autodetachment model [52]. The negative ion lifetime is close to the charge transport time in thin film structures [53]. The lifetime of negative ions depends on the electron energy and temperature; a characteristic dependence for phenanthrene quinone is plotted in Fig. 11b [48].

It should be noted that negative ions can be formed not only in the vibration excitation region but also in various regions of electronic level excitation [48–50] due to different production mechanisms of such ions: vibrational Feshbach resonances are formed in the region of thermal electron energies, shape resonances, in the region from thermal

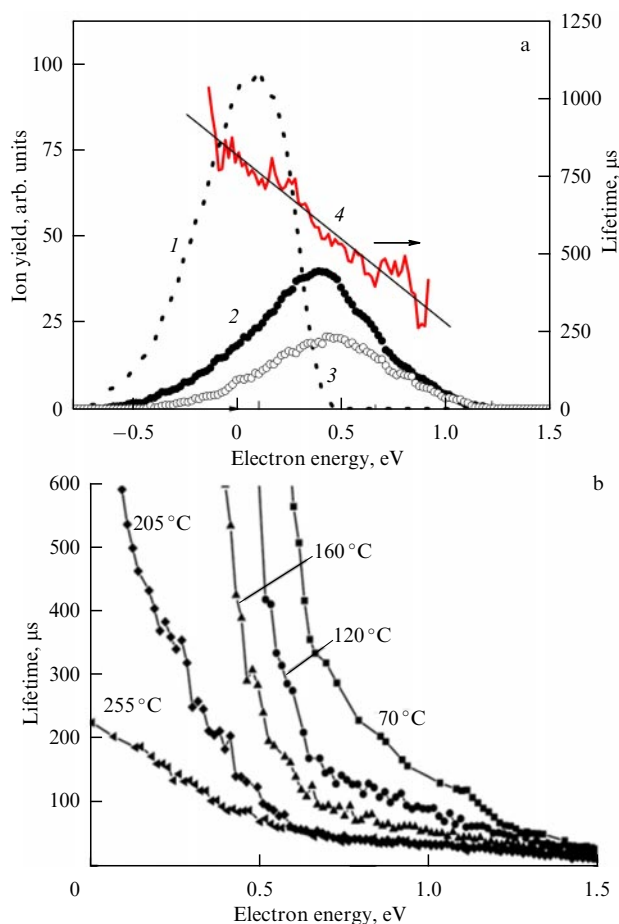


Figure 11. Energy dependences for the production of negative ions: (a) Alq_3 (1 — $\text{SF}_6^-/\text{SF}_6$ yield, 2 — $\text{Alq}_3^-/\text{Alq}_3$ yield, 3 — Alq_3 after autodetachment, 4 — Alq_3^- lifetime) [47]. (b) Energy dependences of the lifetime of negative phenanthrene quinone ions at different temperatures [48].

energies to electronic level excitation energies, and dissociative attachment, at higher energies [52]. Dissociative attachment subsequently leads to the dissociation of the molecule into fragments [48–50]. Studies of a number of other molecules are presented in Refs [54–58].

Studies conducted on the production and properties of negative ions in the gas phase give an idea of their appearance in solids, which manifests itself in the formation of a space charge as well as in hopping charge transport. The transmission of electrons through thin films of organic compounds makes it possible to determine the range of electrons ($1/(n\sigma)$), where n is the density of molecules, σ is the total interaction cross section) and make a comparison with gas-phase data, as well as to study recombination and the formation of a space charge.

In general, it should be noted that the addition or removal of an electron leads to strong changes in the energies of molecular orbitals [59], thereby exerting a strong influence on the transport and recombination properties. Positive and negative ions appear, as a rule, in excited states. The weakening of the bond leads to an increase in the probability of dissociation of these molecules or to a rearrangement of their structure.

3. Conclusions

Owing to the use of a set of stable luminescent organic compounds in the studies, a fairly complete understanding of low-energy electron interaction with large organic molecules has been obtained. As one can see from the small amount of data presented, spectroscopic methods are highly effective for studying a wide range of phenomena occurring during electron-molecular interactions and allow a deeper understanding of the mechanisms of electron energy conversion by such molecules, in particular, by biological ones, as well as in molecular electronics devices. Common features and differences between optical and electronic excitation are shown.

The results of the research outlined in this paper will be useful for understanding the conversion of electron energy by organic molecules in electronics, biology, and plasma chemistry. However, further development of the research area presented here calls for improving experiments, determining the total cross sections of ongoing processes, studying their angular dependence, etc.

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